

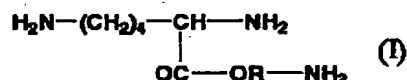
English translation of
JP-A-2002-3462

(54)[Title of the Invention] PRODUCTION METHOD FOR LYSINE
ESTER TRIISOCYANATE

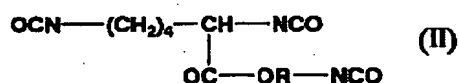
(57)[Abstract]

[Problem] An object of the present invention is to provide a convenient production method for a colorless lysine ester triisocyanate.

[Means for Resolution] The present invention provides a production method for a lysine ester triisocyanate as represented by the general formula (II), in which a triamine as represented by the following general formula (I):



wherein R represents an alkyl, or a salt thereof, and phosgene are allowed to react with each other, to thereby produce a lysine ester triisocyanate as represented by the following general formula (II):



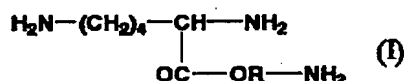
wherein R represents a same meaning as described above, being characterized by comprising the steps of: allowing a mixture comprising the lysine ester triisocyanate as represented by the general formula (II) to be obtained by allowing the triamine as represented by the general formula (I) or the salt thereof

and phosgene to react with each other to come in contact with activated carbon or a metallic halide; and distilling the resultant mixture.

[Claims]

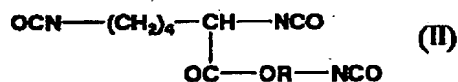
[Claim 1] A production method for a lysine ester triisocyanate as represented by the general formula (II), in which a triamine as represented by the following general formula (I):

[Chemical 1]



wherein R represents an alkyl, or a salt thereof, and phosgene are allowed to react with each other, to thereby produce a lysine ester triisocyanate as represented by the following general formula (II):

[Chemical II]



wherein R represents a same meaning as described above, being characterized by comprising the steps of: allowing a mixture comprising the lysine ester triisocyanate as represented by the general formula (II) to be obtained by allowing the triamine as represented by the general formula (I) or the salt thereof and phosgene to react with each other to come in contact with

activated carbon or a metallic halide; and distilling the resultant mixture.

[Claim 2] The production method as set forth in Claim 1, wherein the salt of the triamine as represented by the general formula (I) is a triamine trihydrochloride.

[Claim 3] The production method as set forth in Claim 1 or 2, wherein the contact with activated carbon or the metallic halide is conducted at from 50 to 150°C.

[Claim 4] The production method as set forth in any one of Claims 1 to 3, wherein the metallic halide is a metallic chloride.

[Claim 5] The production method as set forth in Claim 4, wherein the metallic chloride is zinc chloride.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a production method for a lysine ester triisocyanate useful as a raw material for polyurethane or the like, and a coating agent for a resin or the like.

[0002]

[Prior Art]

While an aliphatic isocyanate can be a product by allowing a corresponding amine or a salt thereof and phosgene to react with each other and then, allowing the resultant

reaction article to be fractionated, the product is sometimes colored in yellow or the like. When the aliphatic isocyanate is used in an application such as a paint or the like, such coloring comes to be a large problem.

[0003]

Conventionally, as a production method for a colorless lysine ester triisocyanate, a method as described in JP-B No. 4-66863 or the like has been known. JP-B No. 4-66863 discloses the production method for the lysine ester triisocyanate which is characterized in that, prior to reacting with phosgene, a lysine monoalkyl ester trihydrochloride is subjected to a pretreatment in which, after the lysine monoalkyl ester trihydrochloride is dispersed in an aqueous non-compatible organic solvent, the resultant dispersion is filtered to separate a filter cake and, then, the thus-separated filter cake is rinsed, dispersed again in the aqueous non-compatible organic solvent to prepare the lysine monoalkyl ester trihydrochloride and, then, the thus-prepared lysine monoalkyl ester trihydrochloride is allowed to react with phosgene in the presence of an inert organic solvent to obtain a reaction liquid and, thereafter, solvent and tar are sequentially removed from the thus-obtained reaction liquid and, subsequently, the resultant liquid is subjected to a thermal treatment at from 100 to 200°C and, then, to a fractionation.

[0004]

However, the above-described method is not practically satisfactory from the standpoint of an industrial production, since there are many steps of handling a large amount of powder or slurry such as dispersing the lysine monoalkyl ester trihydrochloride (powder) into the aqueous non-compatible organic solvent, separating by filtration and, then, rinsing the filter cake and, further, it is necessary to perform distillation steps twice, namely, a tar-removing step and a fraction step.

[0005]

[Problems that the Invention is to Solve]

An object of the present invention is to provide a convenient production method for a colorless lysine ester triisocyanate.

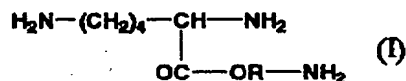
[0006]

[Means for Solving the Problems]

[0007]

The present invention provides a production method for a lysine ester triisocyanate as represented by the general formula (II), in which a triamine as represented by the following general formula (I):

[Chemical 3]

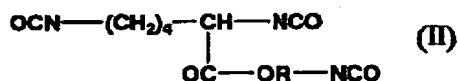


[0008]

wherein R represents an alkyl, or a salt thereof, and phosgene are allowed to react with each other, to thereby produce a lysine ester triisocyanate as represented by the following general formula (II):

[0009]

[Chemical 4]



[0010]

wherein R represents a same meaning as described above, being characterized by comprising the steps of: allowing a mixture comprising the lysine ester triisocyanate as represented by the general formula (II) to be obtained by allowing the triamine as represented by the general formula (I) or the salt thereof and phosgene to react with each other to come in contact with activated carbon or a metallic halide; and distilling the resultant mixture. Hereinafter, such triamines as represented by the general formula (I) and such lysine ester triisocyanates as represented by the general formula (II) are simply referred to also as "triamine" and "lysine ester triisocyanate", respectively.

[0011]

[Mode for Carrying Out the Invention]

In regard to definitions of groups in the general

formulas (I) and (II), an alkylene represents a linear or branched alkylene having from 2 to 6 carbon atoms; for example, ethylene, propylene, butylenes, heptylene, isobutylene, pentylene or hexylene is mentioned, and ethylene is preferred thereamong.

[0012]

In the production method according to the present invention, as for a salt of a triamine to be used as a raw material, for example, an inorganic acid salt such as a hydrochloride, a sulfate or a nitrate, or an organic acid salt such as a p-toluene sulfonate is mentioned, and a hydrochloride is preferred thereamong and a triamine is more preferably in a form of a trihydrochloride thereof. Hereinafter, the production method according to the present invention is described in detail.

[0013]

The triamine or the salt thereof to be a raw material can be produced in accordance with a method as described in, for example, JP-A No. 5-65253. For example, a lysine hydrochloride and an amino alcohol or a hydrochloride thereof are subjected to an esterification reaction in a hydrochloride gas flow while removing moisture under a reduced pressure and, then, an article isolated from the resultant reaction liquid by a crystallization technique by using an alcoholic solvent such as methanol, ethanol, propanol, isopropanol or butanol,

or the like can be used for a reaction with phosgene. Further, optionally, such article which has been re-crystallized or subjected to a dehydration treatment may be used for the reaction with phosgene.

[0014]

The reaction between the triamine or the salt thereof and phosgene is performed in accordance with a method as described in, for example, JP-B No. 60-26775 such that the triamine or the salt thereof is dispersed in an inert solvent such as an aromatic hydrocarbon (for example, benzene, toluene, o-xylene, m-xylene or p-xylene), a chlorinated aromatic hydrocarbon (for example, chlorobenzene, o-dichlorobenzene, m-dichlorobenzene or p-dichlorobenzene), a chlorinated aliphatic hydrocarbon (for example, trichloroethane) or a chlorinated alicyclic hydrocarbon (for example, chlorocyclohexane) preferably at from 80 to 150°C while circulating phosgene in the resultant dispersion. After the reaction, the solvent is optionally removed from the resultant reaction liquid by distillation under a reduced pressure or the like. Phosgene is preferably used in an amount of from 5 to 15 equivalent weight against an amino group of the triamine or the salt thereof.

[0015]

Next, a mixture comprising a lysine ester triisocyanate to be obtained by the above-described reaction is allowed to

come in contact with activated carbon or a metallic halide. Activated carbon or the metallic halide may be added either before or after such removal of the solvent from the reaction liquid. As for a method of the contact, a batch system is preferred, but a packed column may also be used. As for activated carbon, any type of activated carbon is permissible so long as it does not contain moisture and, ordinarily, a commercial product can be used. Such commercial products are available from, for example, Takeda Chemical Industries, Ltd. under the trade name of "Purified Shirasagi" or "Shirasagi P", and Futamura Chemical Co., Ltd. under the trade name of "Taiko SA1000".

[0016]

The metallic halide may either be a highly purified one or that of an industrial grade and is, ordinarily, available in the market. As for a metal in the metallic halide, copper, zinc, aluminum, tin or lead is preferred and, as for a halogen therein, a fluorine, chlorine, bromine or an iodine is mentioned. Specifically, metallic halides such as zinc chloride, aluminum chloride, tin chloride and the like are preferred, and zinc chloride is more preferred thereamong.

[0017]

Activated carbon and the metallic halide may simultaneously be used and such simultaneous use is more effective. An amount of activated carbon or the metallic

halide to be used is, base on the weight of the lysine ester triisocyanate, preferably from 0.1 to 10% by weight and, more preferably, from 0.5 to 7% by weight. When activated carbon and the metallic halide are simultaneously used, they are respectively used preferably in an amount of from 0.1 to 0.8% by weight and, more preferably, in an amount of from 0.3 to 0.6% by weight.

[0018]

A temperature at which activated carbon and the metallic halide are in contact with each other is preferably from 50 to 150°C, more preferably from 70 to 140°C and, still more preferably, from 100 to 140°C. The above-described contact is ordinarily conducted for from 30 minutes to 3 hours under an atmosphere of nitrogen. A pressure at the time of the contact may be under a normal pressure; however, the contact under pressure or reduced pressure is also permissible.

[0019]

The mixture comprising the lysine ester triisocyanate to be obtained by the above-described contact is further distilled; however, before such distillation, it is preferable to remove activated carbon or the metallic halide by filtration or the like. The distillation can be performed by an ordinary method; however, it is preferable to perform a thin-film distillation by using a molecular still. When the thin-film distillation is performed, a pretreatment under a reduced

pressure may optionally be performed thereon before the thin-film distillation.

[0020]

The production method according to the present invention is small in the number of steps of handling powder or slurry and also small in frequencies of distillations and, therefore, is the production method for the lysine ester triisocyanate appropriate for an industrial production. The lysine ester triisocyanate to be obtained by the production method according to the present invention is highly pure, scarcely colored and seldom causes discoloration (for example, yellow discoloration) along the passage of time.

[0021]

Further, the lysine ester triisocyanate to be obtained by the production method according to the present invention is useful for, for example, a coating agent for a polycarbonate resin (as described in JP-A No. 60-63232).

[0022]

[Examples]

Example 1: (1) Production of crude lysine diisocyanate β -isocyanate ethyl ester

100 g of a lysine β -aminoethyl ester trihydrochloride to be obtained in Reference Example 1 was mixed with 500 g of o-dichlorobenzene and, then, a phosgene gas was blown in the resultant mixture at a flow rate of 3 mol/lysine β -aminoethyl

ester trihydrochloride/hour for 12 hours while heating the mixture at 130°C. Thereafter, a nitrogen gas was blown in the resultant mixture for purging phosgene and, subsequently, o-dichlorobenzene was distilled off at from 50 to 120°C under 1.3 kPa, to thereby obtain 100 g of a crude lysine diisocyanate β -isocyanate ethyl ester having a purity of 80%.

[0023]

(2) Purification of crude lysine diisocyanate β -isocyanate ethyl ester

100 g of the crude lysine diisocyanate β -isocyanate ethyl ester obtained in (1) was added with 5 g of activated carbon (trade name: Shirasagi P; available from Takeda Chemical Industries, Ltd.) and, then, heated for 2 hours at 130°C. Thereafter, the resultant mixture was subjected to filtration to remove activated carbon and, subsequently, distilled at 140°C under a pressure of 6.6 Pa by using a falling thin-film molecular still [(trade name: Shibata Molecular Still (TYPE MS-300; available from Shibata Scientific Instruments Co., Ltd.) which was also used in Examples and Comparative Examples as described below), to thereby obtain 60 g of a lysine diisocyanate β -isocyanate ethyl ester. Purity of the thus-obtained lysine diisocyanate β -isocyanate ethyl ester was 99% or more and hue (APHA) thereof was 20.

[0024]

The purity of lysine diisocyanate β -isocyanate ethyl

ester obtained in each of Examples 1 to 3 and Comparative Examples 1 and 2 was analyzed by a method as described below by using a high performance liquid chromatography (HPLC).

(Preparation of sample for HPLC analysis and analysis method)

- 1) About 1.5 ml of aniline was put in a sample bottle.
- 2) Further, about 50 mg of the lysine diisocyanate β -isocyanate ethyl ester was put in the sample bottle and, then, weighed.
- 3) After about 1 ml of acetonitrile was added thereto, the resultant mixture was left still for 5 minutes and, then, added with 200 mg of benzophenone as an internal reference substance.
- 4) The resultant mixture was added with 100 ml of a diluent solvent (ethanol/acetonitrile: 2/1) and, further, added with 50 μ l of a 85% aqueous phosphoric acid solution and, then, allowed to be dissolved.
- 5) 1 ml of the thus-prepared sample solution was taken out of the sample bottle and diluted with 5 ml of the diluent solvent (ethanol/acetonitrile: 2/1) and, then, put on analysis by the HPLC.

(Analysis condition of HPLC)

column: YMC A312 (trade name; available from YMC Co., Ltd.; size: 6x150 mm);

column temperature: 35°C

mobile-phase: acetonitril/methanol/5% aqueous

phosphoric acid solution: 4/1/5 (ratio by volume);

flow rate: 2 ml/min; and

detection: UV (240 nm).

[0025]

Example 2

100 g of the crude lysine diisocyanate β -isocyanate ethyl ester obtained in (1) of Example 1 was added with 5 g of zinc chloride and, then, heated for 2 hours at 130°C. Thereafter, the resultant mixture was subjected to filtration to remove zinc chloride and, subsequently, distilled at 140°C under a pressure of 6.6 Pa by using the falling thin-film molecular still, to thereby obtain 65 g of a lysine diisocyanate β -isocyanate ethyl ester. Purity of the thus-obtained lysine diisocyanate β -isocyanate ethyl ester was 99% or more and hue (APHA) thereof was 30.

[0026]

Example 3

100 g of the crude lysine diisocyanate β -isocyanate ethyl ester obtained in (1) of Example 1 was added with 0.5 g of activated carbon (trade name: Shirasagi P; available from Takeda Chemical Industries, Ltd.) and 0.5 g of zinc chloride and, then, heated for 2 hours at 130°C. Thereafter, the resultant mixture was subjected to filtration to remove activated carbon and zinc chloride and, subsequently, distilled at 140°C under a pressure of 6.6 Pa by using the falling thin-film molecular still, to thereby obtain 63 g of a lysine diisocyanate β -isocyanate ethyl ester. Purity of the

thus-obtained lysine diisocyanate β -isocyanate ethyl ester was 99% or more and hue (APHA) thereof was 20.

[0027]

As is observed in Examples 1 to 3, by the production method according to the present invention, a scarcely colored lysine ester triisocyanate of high purity was able to be produced.

Comparative Example 1

100 g of the crude lysine diisocyanate β -isocyanate ethyl ester obtained in (1) of Example 1 was heated for 2 hours at 130°C and, then, distilled at 140°C under a pressure of 6.6 Pa by using the falling thin-film molecular still, to thereby obtain 70 g of a lysine diisocyanate β -isocyanate ethyl ester. Purity of the thus-obtained lysine diisocyanate β -isocyanate ethyl ester was 97% and hue (APHA) thereof was 200.

[0028]

Comparative Example 2

100 g of the crude lysine diisocyanate β -isocyanate ethyl ester obtained in (1) of Example 1 was heated for 4 hours at 130°C and, then, distilled at 140°C under a pressure of 6.6 Pa by using the falling thin-film molecular still, to thereby obtain 68 g of a lysine diisocyanate β -isocyanate ethyl ester. Purity of the thus-obtained lysine diisocyanate β -isocyanate ethyl ester was 97% and hue (APHA) thereof was 180.

[0029]

Reference Example 1

102 g of lysine monohydrochloride and 109 g of ethanol amine were mixed with each other and, then, a hydrochloric acid gas was blown in the resultant mixture in an amount corresponding to 1.2 mol/ethanol amine for 2 hours. Then, while the pressure was adjusted to be 33 kPa at 120°C, the hydrochloric acid gas was further circulated in the resultant mixture at a rate of 0.2 L/mol lysine/min and held for 7 hours. After such reaction as described above, the resultant reaction solution was subjected to crystallization by using a mixed solvent of methanol and n-butanol and, then, subjected to filtration to obtain a filter cake. The thus-obtained filter cake was dried under a reduced pressure of 66 Pa at 60°C, to thereby obtain 100 g of a lysine β -aminoethyl ester trihydrochloride.

[0030]

[Advantage of the Invention]

According to the present invention, a convenient production method for a colorless lysine ester triisocyanate can be provided.